The role of the grain boundary at chemical and isotopic fronts in marble during contact metamorphism: microscale isotopic zoning in calcite

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Introduction

In a contact aureole in the Hida metamorphiJ terrain, isotopic zoning in calcite shows evidence that oxygen isotopes in grain boundaries are exchanged with metamorphic fluid preferentially with respect to carbon isotopes (Arita and Wada, 1990). This shows that molecular water is an important medium for mass-transportation along grain boundaries during contact metamorphism.

In the central part of the Hida metamorphic terrain, the Utsubo granite intruded into gneiss and crystalline limestone, in an oval shape about 4 km wide and 12 km long. Along fractures in marble,
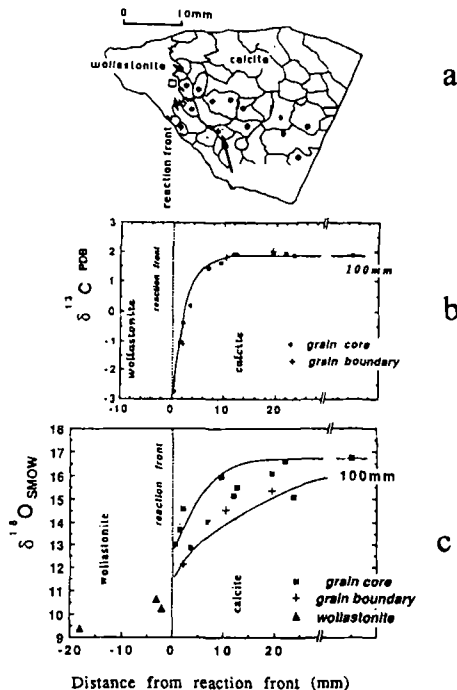
a

b

c

Distance from reaction front (mm)

FIG. 1. Carbon and oxygen isotopic profiles along a traverse at reaction front of marble where wollastonite formed during a contact metamorphism, the Hida metamorphic belt, central Japan. a, Sampling localities of isotopic results; b, carbon isotopic profile, c; oxygen isotopic profile.

wollastonite was formed by reaction with silica in metamorphic fluid emanating from a granite. Calcite grains are roughly equigranular, and wollastonite occurs as acicular crystals in sharp contact with calcite (Fig. 1a). The chemical reaction front is normally sharp and distinctive as shown in Fig. 1. In microscale, the grain boundary seems to have been an important conduit of metasomatic fluid flow, because wollastonite preferentially crystallized along the grain boundary at the front. This shows that the metamorphic fluid invaded into the calcite crystal along the grain boundary, but the reaction rate was fast enough to make a distinct chemical front.

Here, we present carbon and oxygen isotopic data from a metasomatic front in marble from the Hida metamorphic belt, central Japan, showing a typical isotopic zonation outward in marble. At micrometer to millimeter scales, carbon and oxygen isotopic zoning show different behaviours.

Analytical procedure

For determination of carbon and oxygen isotope ratios of the core and rim of individual calcite grains, pulverized samples were obtained by scraping using a keen knife edge from a polished surface stained with Alizarin-S. Carbon and oxygen isotope compositions in narrow zones of calcite–calcite grain boundaries were prepared precisely by a step-by-step splitting technique using an electric freezing microtome (Wada, 1988). Samples thus prepared were reacted with concentrated phosphoric acid at $60°C$ in vacuo to liberate CO_2 (Wada et al., 1982, 1984). The oxygen isotopic ratio in wollastonite was analyzed by a conventional bromine pentafluoride extraction technique at Misasa Laboratory at Okayama University.

Isotopic results and discussion

Carbon and oxygen isotopic results are shown in Figs. 1b and c. The sampling locality is shown in Fig. 1a. Along a traverse perpendicular to the
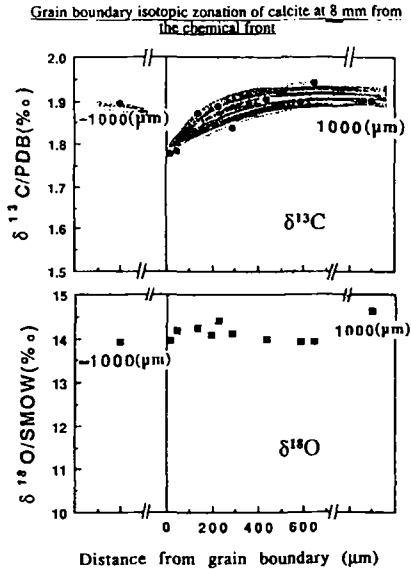
FIG. 2. Grain boundary isotopic zonation of calcite at 8 mm from the chemical reaction front. Sample locality is indicated in Fig. 1a.

chemical front, $\delta^{13}C$ values of calcite grains show a steep isotopic gradient from $-2.8‰$ to $+1.9‰$ within 10 mm of the chemical front and level off at a constant value of $+1.9‰$. Three data points from grain boundaries of calcite crystals fall on the fit curve, although the sample collected about 2 mm from the chemical front was slightly lower relative to the core values. $\delta^{18}O$ values of calcite along the traverse also showed a steep isotopic gradient with scatter, but in contrast to $\delta^{13}C$, $\delta^{18}O$ values from the grain boundary were lower than those of the adjacent grain cores. Such an oxygen isotope trough at the grain boundary has already been reported in this same area by Arita and Wada (1990), and could be traced regionally to marble about 1 km from the granite contact. The $\delta^{18}O$ values of wollastonite also show an isotopic gradient with heavy values at the reaction front and light value far from the front (Fig. 1c). The oxygen isotopic fractionation between calcite and wollastonite in the narrow zone near the chemical front may be mostly in isotopic equilibrium, based on the experimental equilibrium fractionation of Chiba et al. (1989).

We measured the carbon and oxygen isotopic values in two calcite grain boundary profiles, about 2 and 8 mm from the chemical reaction front, respectively. The $\delta^{13}C$ profile 2 mm from the reaction front represents deep penetration into the calcite grain and shows an increase in the core of about 1‰, which is consistent with the carbon isotopic profile along the traverse in Fig. 1b. On the

other hand, the $\delta^{18}O$ profile (Fig. 1c) shows no apparent gradient within 1 mm of the grain boundary, varyng between 13 and 14‰. This probably indicates complete oxygen exchange with metamorphic fluid over this 1 mm distance. At 8 mm from the chemical reaction front, the carbon isotopic profile shows a steep gradient only within 200 μm of the boundary and levels off at a constant value of $+1.9‰$ (Fig. 2) . The oxygen isotopic profile indicates deep penetration into the calcite grain, to about 700 μm and has an isotopic gradient extending 1 mm into the core. As shown in these results, the carbon isotopic profile along the traverse shown in Fig. 1b reflects the grain core profile, but at smaller scales the very rim of the calcite grain demonstrates a small carbon isotopic trough.

The oxygen isotope profile along the traverse shows a large isotopic difference between the grain core and the rim parts in the individual calcite grains. This difference shows that oxygen-containing media penetrated more easily than carbon past the grain boundary for elementary exchange in the calcite rim. During wollastonite formation, a large amount of carbon dioxide should be produced at the chemical front. Normally the mole fraction of water in the hypothesized metamorphic fluid (CO_2–H_2O system) during the formation of wollastonite is high (Inazuki, 1982; Okui, 1985). Only water molecules preferentially penetrated along the grain boundary by diffusion. The CO_2 generated from the reaction at the chemical front penetrated only a limited amount. Carbon species such as CO_2 or CO_3^- ions in metamorphic fluid should migrate into crystalline marble mainly through body or lattice diffusion. On the other hand water molecules can penetrate into the grain by grain boundary diffusion.

As shown in the carbon and oxygen isotopic profiles, the fit curves calculated using an infinite one dimensional diffusion model reveal the diffusion coefficients. Assuming a constant temperature and duration during formation of the carbon and oxygen profiles, the oxygen isotopic diffusion coefficient for water molecules, probably by lattice diffusion, is 6 times larger than the carbon isotopic diffusion coefficient for CO_2 or CO_3^- by lattice diffusion. On the other hand, the profile of oxygen isotopes showed two diffusion mechanisms, both via water molecules: lattice diffusion and grain boundary diffusion. As shown in Fig. 1c, the crest line of the oxygen isotopic profile of calcite cores may show lattice diffusion and the grain boundary profile may indicate grain boundary diffusion. The calculated diffusion coefficient for the grain boundary is about 7 times larger than that of lattice diffusion.